

1054,620



PATENT SPECIFICATION

1054,620

NO DRAWINGS

Date of Application and filing Complete Specification: Dec. 2, 1965.

No. 51208/65.

Application made in Canada (No. 918,509) on Dec. 11, 1964.

Complete Specification Published: Jan. 11, 1967.

© Crown Copyright 1967.

Index at acceptance:—C3 P (2C8C, 2D1A, 2K7, 2T2A); C1 AK4

Int. Cl.:—C 08 d 13/28 // C 01 b

COMPLETE SPECIFICATION

Vulcanizates having improved Ageing Properties

5 We, POLYMER CORPORATION LIMITED, a company organised under the laws of Canada, of Sarnia, Ontario, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to vulcanizable compositions of rubbery polymers having improved resistance to ageing. In particular, it relates to mixtures of rubbery polymers and carbon blacks.

15 It is known that rubbery polymers may be admixed with carbon blacks and vulcanizing agents and the mixture vulcanized to produce useful products having high strength and satisfactory ageing properties at room temperature. However, under service at elevated temperatures these vulcanizates deteriorate; 20 for example, natural rubber or polyisoprene soften, thus losing tensile strength and decreasing in modulus of elasticity; on the other hand, butadiene-1,3 rubbers harden, also losing tensile strength but increasing in modulus. 25 The utility of such products is thus limited. Incorporation of anti-degradants has provided some improvement but further success in preventing such deterioration is sought by the art, especially with the increasing severity of 30 modern applications.

The object of the present invention is to provide rubbery compositions having improved resistance to ageing.

35 The object of the invention is achieved in the process of preparing a reinforced vulcanizate of a rubbery diolefin polymer which comprises vulcanizing a mixture of said polymer with vulcanizing agents and carbon black by the improvement which comprises using 40 a modified carbon black, the modification being effected by reacting an unmodified black having at least 1% by weight of non-aqueous volatile matter, a surface area of 60 to 400 square meters per gram and a particle diameter of between 10 and 50 millimicrons with 45

an amine selected from the group represented by the formulae



wherein R is an alkylene radical having 2 to 5 carbon atoms, said modified black having essentially no free amine and containing 0.5 to 5.0 parts combined nitrogen per 100 parts by weight of modified black. 50

One embodiment of the invention involves 55 an improvement in the process of preparing a reinforced vulcanizate of a rubbery polymer of a $\text{C}_4\text{—C}_8$ open chain diolefin which comprises vulcanizing a mixture of said polymer with vulcanizing agents and carbon black, 60 said improvement comprising using a modified carbon black, the modification being effected by reacting an unmodified black having 1—8% by weight of non-aqueous volatile matter, a particle diameter between 10 and 65 50 millimicrons and a surface area of 60—400 square meters per gram with an amine selected from the group represented by the formulae



wherein R is an alkylene radical having 2 to 5 carbon atoms, said modified black having essentially no free amine and containing 0.5—5.0 parts combined nitrogen per 100 parts by weight of modified black. 75

In another preferred embodiment, the unmodified black has a volatile content of between about 3 and 8% by weight, a surface area of about 100—400 square meters per gram, a particle diameter of about 10—35 80 millimicrons, a pH of an aqueous slurry of about 3—5 and is modified by reaction with 1,2-propylene diamine, 1,3-propylene diamine or 3,3'-diamino dipropylamine, whereby the modified black contains no free amine but 85 contains 0.5—5.0, preferably 1.5—3.5 parts,

nitrogen per 100 parts by weight of modified black.

In another preferred embodiment, the unmodified black has a volatile content of between about 1 and 5% by weight, a surface area of about 60—200 square meters per gram, a particle diameter of about 20—50 millimicrons, a pH of an aqueous slurry of about 7—9, and is modified by reaction with 1,2-propylene diamine, 1,3-propylene diamine or 3,3'-diamino dipropylamine, whereby the modified black contains no free amine but contains 0.5—5.0, preferably 1.5—3.5 parts, nitrogen per 100 parts by weight modified black.

The rubbery polymers which may be used in this invention include natural Hevea rubber and synthetic rubbery homopolymers of open chain conjugated diolefins or copolymers thereof with copolymerizable monomers having the vinylidene group, $H_2C=G<$. Examples of the conjugated diolefins are the C_4-C_8 open chain diolefins such as butadiene-1,3-isoprene, 2,3-dimethyl butadiene, and 2-chlorobutadiene. The copolymers contain at least 60 per cent by weight of diolefin units. The copolymerizable monomers include acrylonitrile, styrene, alpha-alkyl styrene, vinyl pyridine and the C_1-C_4 alkyl acrylates. The synthetic polymers may be produced by any suitable means such as by emulsion or by solution polymerization techniques, such techniques and polymers being known in the art and not the subject of the invention. A preferred rubbery polymer is a copolymer of butadiene-1,3 with up to 40% by weight styrene, for example one having a butadiene/styrene ratio of about 75/25. Blends of various rubbery polymers may also be employed in the practice of this invention if desired.

The carbon blacks which are used in the practice of this invention are those which have been oxidized to a non-aqueous volatile matter content of at least one per cent by weight, have a surface area of from 60 to 400 square meters per gram, and have a particle diameter of from 10 to 50 millimicrons. Such oxidized blacks are known and are produced by known processes such as channel impingement and furnace combustion, using feed stocks of either gas or oil. Furnace blacks having less than one per cent volatile content and of the so-called thermal type do not provide the advantages of the invention and are not included.

The properties of carbon black may be determined by known methods generally described as follows. The characteristics as reported herein were determined as follows: specific surface area was determined by nitrogen absorption using the method of Brunauer-Emmett-Teller; the particle diameter was taken as the arithmetic mean diameter as measured from electron micro-

graphs by known methods; the oil absorption value, in pounds of oil per 100 pounds of black, is given herein as measured by the Cabot Coherent Ball Method using a standard linseed oil; the volatile content is a measure of the carbon-oxygen complexes present on the carbon surface, which are decomposed into gaseous products when the black is heated for 7 minutes at 950° C; the percentage of fixed carbon is taken as 100 minus the percentage of volatile matter; the pH value as used herein is the value determined with the glass electrode in a carbon black-water sludge (ASTM D1512—57T). The chemisorbed oxygen is believed to be present on the carbon surface in the form of carbon-oxygen complexes such as quinone, carboxyl, aldehyde, and hydroxyl groups.

The amines which may be used in the practice of this invention may be generally described as polyamines derived from lower monoolefins, generally ethylene or propylene. More specifically the amines are those selected from the group represented by the structural formula



or the group represented by the structural formula



where R is an alkylene radical having 2 to 5 carbon atoms. Examples of the former are ethylene diamine, 1,3-propylene diamine, and 1,2-propylene diamine while examples of the latter are diethylene triamine (also known as 2,2'-diamino diethylamine) and dipropylene triamine (also known as 3,3'-diamino dipropylamine).

The amount of amine employed is such as to result in a modified black having 0.5 to 5.0 per cent by weight of nitrogen chemically combined. The optimum amount of a specific amine to be used with a particular carbon black may be determined by those skilled in the art and it is preferred that the modified black contain about 1.5 to 3.5% by weight nitrogen.

The modification of the carbon black may be accomplished by reaction with the amine in the gaseous state at an elevated temperature, preferably in a closed system, to avoid loss of the amine. The modification may also be effected by contacting the black with a solution of amine, preferably at a temperature between the boiling point of the amine (if less than that of the solvent) and about the boiling point of the solvent medium. The solvent may be water, alcohol, benzene, hexane, etc., the choice being guided by such factors as solubility of amine, boiling point, chemical stability, and the like as would be obvious to those of the art. Although the contact time of the black with the amine is somewhat dependent on the particular amine and on the temperature, the process is generally completed in about one to two

hours. After treatment of the black by the amine, excess or free amine is removed by any suitable process such as washing and evaporation under vacuum.

- 5 As indicated above, the process of modifying the carbon black may vary, and the following three methods were used successfully by the applicants:

A.—*Gaseous Treatment*

- 10 Carbon black and amine were placed in a stainless steel, thermostatically-controlled autoclave equipped with a pressure rupture disc. The amount of amine introduced was chosen so as to be in excess of that required to result in the desired content of nitrogen in the modified black. The temperature of the contents of the autoclave was then raised to 50—60° C above the boiling point of the amine. After a period of not less than one hour, the pressure on the autoclave was released, but the temperature maintained so as to expel unreacted amine and any vapor of reaction by-products. After cooling to room temperature, the modified black was removed, ball-milled to break up any lumps, passed through a 25—50 mesh sieve, and finally dried at an elevated temperature to remove traces of free amine. When modified black was pyrophoric in nature, it was mixed with a minor amount of powdered "dry-ice" (solid carbon dioxide) before ball-milling and sieving.

B.—*Aqueous Treatment*

- 35 The amine was dissolved in distilled water (one mole per litre) and placed in a three-necked, round bottomed flask equipped with a suitable paddle-type stirrer, thermometer, and reflux condenser. The desired quantity of carbon black was introduced while stirring. Heat was supplied by an electric heating mantle to maintain a temperature of 100° C. The mixture was kept under reflux for about two hours. On cooling, the modified carbon black was filtered from the solution, washed with distilled water 3—5 times to remove free amine, and then dried.

C.—*Treatment in Organic Solvent*

- 50 This method was essentially the same as that employed in B except that an organic solvent, such as toluene, was substituted for the water, and the temperature adjusted to the boiling point of the solvent.

- 55 The compounding of the carbon black and rubbery polymer together with a desired formulation of various materials such as another pigment additive, softener or plasticizer, vulcanizing agents such as zinc oxide, sulfur, and accelerator such as mercaptobenzothiazole or thiuram sulfide is widely known and practised in the art, as is the shaping, and vulcanizing operation. In general practice in the art, about 25—75 parts by weight of carbon black per 100 parts of polymer are used, but this quantity may be varied considerably as determined by the end use

of the article to be produced. Uses for goods produced from rubber materials of this invention include: hoses and tubes, transmission belts, tire treads, wire insulation, and the like.

The following examples illustrate specific embodiments of the present invention:

EXAMPLE I

Three amines were reacted with a carbon black which is marketed under the trademark ELF-1*, in some cases using the gaseous method outlined under Procedure A, and in other cases using Procedure B. The modified blacks were analyzed for nitrogen content. The quantities of amine and maximum temperatures used were:

Procedure A—1,2-propylene diamine, 1 mole per 125 grams black, at 200° C	75
1,3-propylene diamine, 3 moles per 300 grams black, at 225° C	85
ethylene diamine, 1 mole per 125 grams black, at 200° C	80
Procedure B—3,3 - diaminodipropylamine, 0.4 mole per 250 grams black, at 100° C	90
1,3 - propylene diamine, 1 mole per 250 grams black at 100° C.	95

*ELF-1, a product of Godfrey L. Cabot Inc., is described as a fluffy channel black having the following properties:

Estimated surface area (square meters per gram)	120	100
Average particle diameter (microns)	23	
Oil absorption (pounds oil per 100 pounds black)	125	
Volatile content (%)	5	105
Fixed carbon (%)	95	
pH	5.0	
Apparent density (pounds per cubic foot)	13	

In each case the modified black was admixed with a commercial butadiene-styrene rubber containing about 28% bound styrene and the mix compounded on a laboratory mill according to the following recipe, in parts by weight:

Polymer	100	
Modified black	40	
#NBS grade zinc oxide	5.0	
#NBS grade sulphur	2.0	
#NBS grade Benzo-thiazyl disulfide	1.75	120

From the compounded stock, tensile sheets were cured for 100 minutes at 145° C. The stress-strain properties of some were measured immediately whereas others were air-aged in an oven at 100° C for periods up to 5 days, after which time their stress-strain properties were measured. The test data for

#Nation Bureau of Standards

the unaged and aged specimens, together with test data for specimens from a control sample containing unmodified carbon black, are shown in Table I.

5 These data show that (a) superior physical properties were obtained on the unaged samples when the modified black was used instead of the unmodified black, and (b) a much superior balance of physical properties was retained after ageing by the samples containing the modified black.

A control experiment was also performed in which unmodified ELF-1 carbon black was mixed with the rubbery polymer, and the mixture then mixed with 1,2-propylene diamine in the same proportion as shown under Procedure A for this example. The result was a deteriorated mass having properties essentially useless for the preparation of a vulcanizate. Such observation indicates that the advantages of the invention are not achieved by the mere presence of amine.

TABLE I

Stress-Strain Properties of Vulcanizates

Type of Amine	NO Amine Treatment	Gaseous Treatment			Aqueous Solution Treatment	
		1,2-propylene, diamine	1,3-propylene diamine	ethylene diamine	3,3-diamino dipropylamine	1,3-propylene diamine
% nitrogen in modified black	0	3.1	3.4	3.7	1.3	2.2
Stress-Strain Tests						
<u>Unaged</u>						
Tensile, (psi)	4005	4940	4025	4760	4800	4725
Elongation at break, (%)	545	590	500	560	510	470
Modulus at 100% elongation, (psi)	345	315	395	320	405	400
<u>Aged at 100°C. in air for 5 days</u>						
Tensile, (psi)	2030	4010	3685	3500	3460	3435
Elongation, %	155	400	335	300	270	270
Modulus at 100%, (psi)	1110	575	755	730	860	895

EXAMPLE II

700 grams of a high abrasion, pelletized, oil furnace black sold by Godfrey L. Cabot Inc. under the trade mark Vulcan-3*, was treated at 266° C with two moles of 1:2 propylene diamine according to Procedure A. The modified black had a nitrogen content of 0.64% by weight. It was compounded

with a butadiene-styrene copolymer and vulcanized and tested along with a control as in Example I. The results which are shown in Table II indicate a much superior retention of properties on ageing for the compounds containing the modified black as compared to those containing the unmodified black.

TABLE II

Physical Tests	No Amine Treatment (Control)	Treatment with 1,2-Propylene Diamine
<u>Unaged</u>		
Tensile, (psi)	4475	4105
Elongation at break, (psi)	450	400
Modulus at 100% elongation, (psi)]	345	450
<u>Aged at 100°C. for 5 days</u>		
Tensile, (psi)	2605	3535
Elongation, (psi)	175	220
Modulus at 100%, (psi)	1080	960

*Vulcan-3 has the following characteristics:

	Estimated surface area (square meters per grams)	74
20	Average particle diameter (milli-microns)	29
	Oil absorption (pounds oil per 100 pounds black)	130
	Volatile content (%)	1.0
25	Fixed carbon (%)	99.0
	pH	8.5
	Apparent density (pounds per cubic foot)	22

EXAMPLE III

Two 700 gram samples of "medium processing" channel black sold by Godfrey L. Cabot Inc. under the trade mark Spheron 6*, were treated by Procedure A with 1,2 propylene diamine. The first sample, (a), was treated with 2 moles of amine at 278° C, and the second sample, (b), was treated with 0.2 moles of amine at 328° C.

The two modified blacks and a control were evaluated in a compound of a butadiene-styrene copolymer as Example I. The results as well as the analysis for nitrogen are shown in Table III.

TABLE III

Wt. % Nitrogen in modified black	1.85	1.0	No Amine (Control)
Stress-Strain Tests			
<u>Unaged</u>	(a)	(b)	
Tensile, (psi)	4490	4085	3800
Elongation, (%)	530	520	490
Modulus at 100%	340	335	340
Aged at 100°C. in air for 5 days			
Tensile, (psi)	2875	2345	1670
Elongation (%)	270	180	130
Modulus at 100%	640	1130	1125

*Spheron 6 has the following characteristics:

	Estimated surface area (square meters per gram)	110
5	Average particle diameter (milli-microns)	25
	Oil adsorption (pounds of oil per 100 pounds black)	115
	Volatile content (%)	5
10	Fixed carbon (%)	95
	PH	4.5
	Apparent density (pounds per cubic foot)	22

15 The data show that the use of the modified black produces compounds having higher tensile strengths than those produced using the unmodified blacks and at the same time the resistance to ageing is greatly improved.

EXAMPLE IV

A "fluffy" carbon black with a high volatile matter content (7—8%) of similar average particle size to that used in Example I, but with a surface area of about 210 square meters per gram, was treated at 205° C using the gaseous Procedure A and employing 1 mole of 3,3-diamino-dipropylamine per 300 grams of black. The modified black had a nitrogen content of 3.7 per cent. Stress-strain data on aged and unaged cured rubber specimens were obtained as in Example I, for rubber compounded with the amine-treated black and with the untreated black.

The results are shown in Table IV.

TABLE IV

		Unaged	Aged at 100° C. in air for			
			1 day	2 days	3 days	5 days
Tensile (psi)	Unmodified Black	4080	4820	3755	3800	3860
	Modified Black	4400	4300	4355	4085	4105
Elongation (%)	Unmodified Black	560	480	370	350	360
	Modified Black	740	680	680	640	620
Modulus at 100%	Unmodified Black	230	445	510	595	690
	Modified Black	255	275	285	335	390

EXAMPLE V

5 An oxidized furnace carbon black having a calculated average particle diameter of 10 millimicrons, a pH of 3.4, a volatile content of 10%, and oil absorption of 112 pounds oil per 100 pounds black, was treated using Procedure A with 1 mole of 1,2-propylene diamine per 190 grams of black resulting in 2.9% by weight nitrogen per 100 grams

modified black. Vulcanizates prepared using the modified black and the unmodified black were tested as in Example I. 10

From the results shown in Table V, it can be seen that the modified black gives a vulcanizate which, after ageing, gives a higher tensile value and a better balance of stress-strain properties than the vulcanizate prepared using the unmodified black. 15

TABLE V

Physical Tests on Vulcanizate	Oxidized Furnace Carbon Black	
	No Amine Treatment (Control)	Treatment with 1,2 Propylene diamine
<u>Unaged</u>		
Tensile (psi)	5345	4680
Elongation at break (%)	740	540
Modulus at 100% elongation (psi)	245	310
<u>Aged at 100°C. for 5 days</u>		
Tensile (psi)	2315	2830
Elongation (%)	220	280
Modulus at 100% (psi)	855	780

20 WHAT WE CLAIM IS:—

1. In the process of preparing a reinforced vulcanizate of a rubbery diolefin polymer which comprises vulcanizing a mixture of said polymer with vulcanizing agents and carbon black, the improvement which comprises using a modified carbon black, the modification being effected by reacting an unmodified black having at least 1% by weight of non-aqueous volatile matter, a surface area of 60 to 400 square meters per gram and a particle diameter of between 10 and 50 millimicrons with an amine characterized by having the formula



35 wherein R is an alkylene radical having 2 to 5 carbon atoms, said modified black having essentially no free amine and containing 0.5 to 5.0 parts combined nitrogen per 100 parts by weight of modified black.

40 2. The process of claim 1 in which the unmodified black has a non-aqueous volatile content of 1 to 8 percent by weight.

3. The process according to claim 1, in which the unmodified black has a non-aqueous volatile matter content of 3 to 8 percent by weight, a particle size of between 10—35

millimicrons, a surface area of 100—400 square meters per gram, and a pH when in aqueous slurry of 3 to 5.

4. The process according to claim 1, in which the unmodified black has a non-aqueous volatile content of 1 to 5 percent by weight, a particle diameter of 20—50 millimicrons, a surface area of 60—200 square meters per gram, and a pH when in aqueous slurry of 7 to 9. 50

5. The process according to any of claims 1—3 wherein the unmodified black is an oxidized furnace black. 55

6. The process according to any of claims 1—4 wherein the unmodified black is a fluffy black. 60

7. The process according to any of claims 1—6 in which the vulcanizate is prepared from a rubbery polymer of a C₄—C₈ open chain diolefin. 65

8. The process according to claim 7 wherein the polymer is a polymer of butadiene-1,3.

9. The process according to claim 8 wherein the polymer is a copolymer of butadiene-1,3 and styrene. 70

10. The process according to any of claims 1—9 wherein the amine is a diamine derived from an olefine having 2 or 3 carbon atoms.

11. The process according to any of claims 75

- 1—9 wherein the amine is a triamine derived from an olefine having 2 or 3 carbon atoms.
12. The process according to any of claims 1—9 wherein the amine is 1,2-propylene diamine. 5
13. The process according to any of claims 1—9 wherein the amine is 3,3¹ diamino dipropylamine.
14. The process according to any of claims 10 1—13 wherein the modified black contains from 1.5 to 3.5 parts combined nitrogen per 100 parts by weight of modified black.
15. The process of preparing a reinforced vulcanizate from a mixture which comprises 15 a rubbery diolefin polymer, vulcanizing agents, and a modified carbon black, substantially as described herein with reference to the foregoing Examples.
16. A vulcanizate when prepared from a mixture comprising rubbery diolefin polymer, vulcanizing agents and a modified carbon black by the process of any of claims 1—14. 20
17. A vulcanizate when prepared from a mixture comprising a rubbery diolefin polymer, vulcanizing agents, and a modified carbon black substantially as described herein with reference to the foregoing Examples. 25
- For the Applicants:—
A POOLE & CO.,
Chartered Patent Agents.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1967. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.